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(54) Title: COMPOSITIONS AND METHODS OF USING THE SAME

(57) Abstract

The present invention discloses compositions containing a one or more transfer agents and one or more barrier materials which form, upon application to a substrate, even a wet substrate or substrate immersed under water, adhesive, protective barriers. The compositions may be modified to provide an appropriate viscosity and other characteristics and may serve as a carrier for active agents.

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TITLE OF THE INVENTION

COMPOSITIONS AND METHODS OF USING THE SAME

This application claims priority to U.S. Provisional Application Serial Nos. 60/113,950, filed December 24, 1998, and 60/117,283, filed January 26, 1999.

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to compositions and methods of using the same. In particular, the present invention relates to novel protective compositions and methods of treating certain surfaces. In a preferred embodiment, the present invention relates to skin care and specifically to methods of treating the skin, even wet skin or skin which is immersed in water, with compositions, which provide the skin with a protective barrier. The present invention also relates to compositions which provide the skin, even wet skin or skin which is immersed in water, with a protective barrier. The present invention also relates to compositions which can clean and remove contamination from the skin while applying a protective barrier. Throughout this invention, the term "skin" is meant to include not only the exterior integument or dermis/epidermis/stratum corneum of man but also the internal and external surfaces of organs and vessels including wounds, linings, membranous surfaces and glomeruli of man and other animals, and other surfaces such as glass, metal, paint, plastic, and all others which, like skin, can be electrostatically negatively charged.

Discussion of the Background:

Numerous types of skin care compositions are known. For example, skin care compositions are often classified as being either medicated or non-medicated. Other types of skin care compositions include, e.g., sun blockers, moisturizers, etc. However, two general drawbacks of many skin care compositions are that they are difficult or impossible to apply to wet (or sweaty) skin and they are easily removed from the skin. Thus, one goal of the present invention is to provide skin care compositions which provide a long-lasting, protective barrier on the skin. Another goal of this invention is to provide skin care compositions which can effectively and aesthetically be applied to skin which is wet or even immersed under water or aqueous solutions. Yet another goal of this invention is to provide skin care compositions which can effectively and aesthetically be applied to skin to clean and remove contaminants from skin which is wet or even immersed under water or aqueous solutions.

SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide novel skin care compositions.

It is another object of the present invention to provide novel skin care compositions which provide a long-lasting protective barrier on the skin.

It is another object of the present invention to provide a method for treating the skin which confers improved protection to the skin.

It is another object of the present invention to provide novel skin care compositions which can be effectively and aesthetically applied to skin which is wet or even immersed under water or aqueous solutions.

It is another object of the present invention to provide novel skin care compositions which can effectively and aesthetically be applied to skin to clean and remove contaminants from skin which is wet or even immersed under water or aqueous solutions.

These and other objects, which will become apparent during the following detailed description, have been achieved by the inventors' discovery that application of a composition which comprises:

(a) 0.25 to 25 wt.%, based on the total weight of (a) and (b), of one or more transfer agents; and

(b) 75 to 99.75 wt.%, based on the total weight of (a) and (b), of one or more barrier materials,

to the skin results in the formation of a protective barrier on the skin.

The inventors have also discovered that compositions which comprise:

(a′) 65 to 99.75 wt.%, based on the total weight of (a′) and (b′), of one or more barrier materials; and

(b′) 0.25 to 35 wt.%, based on the total weight of (a′) and (b′), of a mixture, said mixture comprising:

(b″) 0.25 to 99.99 wt.%, based on the total weight of (b″) and (b‴), of one or more transfer agents; and

(b‴) 0.01 to 99.75 wt.%, based on the total weight of (b″) and (b‴), of one or more skin care agents,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition,

are useful for applying the skin care agent to the skin.

The inventors have also discovered that compositions comprising:

(1) 25 to 80 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 1 to 50 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 20 to 50 wt.%, based on the total weight of (1), (2), and (3), of water,

are useful for applying the skin care agent to the skin.

The inventors have also discovered that compositions comprising:

(i) 1 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 10 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 1 to 50 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan,

are useful as skin care formulations.

Thus, the present invention provides new compositions which form long-lasting, protective barriers on the skin and can be effectively and aesthetically applied to wet or dry skin, skin which is covered with sweat or other secretions, skin which is soiled or contaminated or skin which is immersed under water or aqueous solutions. The methods of this invention result in the electrostatic bonding of waxy materials to the skin.

The compositions of the present invention may be applied to the skin either by hand or by using any of a variety of skin application appliances, such as an atomizer, spray can, brush, wipe, cotton puff, roll-on device, or other system or device particularly applicable to the specific surface being treated.

The materials used for covering the applicator-ends of the appliance may include, for example: a) natural or synthetic yarn, filaments, or other fibrous material either as such or assembled as a textile, or to any braided, stranded, woven, non-woven, knitted, matted, felted, etc. material, in which the materials of the composition of the present invention (hereinafter MCPI) are held among or between the fibers or the strands of the materials; b) foam-like or otherwise porous materials in which the MCPI are held within pores or apertures; or c) non-porous, non-fibrous materials such as some types of wood, plastic, metal, etc.

Thus, in one embodiment of the present invention, a single monolayer is composed of a low molecular weight transfer agent in which positively charged groups react with the negatively charged surfaces of the skin and the water repelling part of the hydrophobic chain forms a highly hydrophobic interface. Examples of such transfer agents are cetyltrimethylammonium bromide (CTAB), hexadecyltrimethylammonium bromide (HDTAB), 5-amino-1,3-bis(2-ethylhexyl)-5-methylhexahydro-5-methylpyrimidine (hexetidine) and various amines and quaternary amines, of which a good example is Hyamine-1622 quaternary amine.

The compositions of the present invention are generally liquid, semi-solid or solid state materials which may be applied to skin surfaces by hand, by pouring, by injection, or by flowing. For the compositions of the present invention to be applied

through the use of an atomizer, spray can, brush, wipe, cotton puff, roll-on device, or any other applicator or method of application by which liquid, semi-solid, or solid materials may be brought into contact with the skin, it may be necessary to modify the viscosity of the composition with suitable volatile solvents known in the art or to form emulsions by known means to provide formulations of appropriate viscosities.

The compositions of the present invention, as applied to the skin, provide a multi-component protective coating (hereafter called the "Protective Coating: or "PC"), as follows:

(1) The transfer agent component has dual functionality, being composed of materials having some molecular segments or parts of a polymeric chain which are positively charged and other such segments which exhibit hydrophobic characteristics.

(2) The barrier component is a hydrophobic, inert material (hereafter called the "barrier" material), such as a wax or polydimethylsiloxane which mixes with and adheres to the relatively uncharged, hydrophobic molecular segments or parts of the transfer agent molecule. The thickness of the barrier stratum is typically between about 1 and about 10 microns but can be thinner or thicker depending on the requirements of the particular application.

(3) Compositions of the present invention may optionally include one or more active agents which are intended to provide specific medical, cosmetic, or other effects according to the known art relating to such ingredients.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Thus, in a first embodiment, the present invention provides novel compositions which comprise:

(a) 0.25 to 25 wt.%, based on the total weight of (a) and (b), of one or more transfer agents; and

(b) 75 to 99.75 wt.%, based on the total weight of (a) and (b), of one or more barrier materials.

Preferably, the present composition contains:

(a) 1 to 12 wt.%, based on the total weight of (a) and (b), of one or more transfer agents; and

(b) 88 to 99 wt.%, based on the total weight of (a) and (b), of one or more barrier materials.

In a second embodiment, the present invention provides novel compositions which comprise:

(a′) 65 to 99.75 wt.%, based on the total weight of (a′) and (b′), of one or more barrier materials; and

(b′) 0.25 to 35 wt.%, based on the total weight of (a′) and (b′), of a mixture, said mixture comprising:

(b″) 0.25 to 99.99 wt.%, based on the total weight of (b″) and (b‴), of one or more transfer agents; and

(b‴) 0.01 to 99.75 wt.%, based on the total weight of (b″) and (b‴), of one or more skin care agents,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition.

Preferably, in this fifth embodiment, the present composition contains:

(a′) 75 to 99 wt.%, based on the total weight of (a′) and (b′), of one or more barrier materials; and

(b′) 1 to 25 wt.%, based on the total weight of (a′) and (b′), of a mixture, said mixture comprising:

(b″) 1 to 99.9 wt.%, based on the total weight of (b″) and (b‴), of one or more transfer agents; and

(b‴) 0.1 to 99 wt.%, based on the total weight of (b″) and (b‴), of one or more skin care active agents,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition.

In a third embodiment, the present invention provides a method for forming a protective barrier on skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(a) 0.25 to 25 wt.%, based on the total weight of (a) and (b), of transfer agent; and

(b) 75 to 99.75 wt.%, based on the total weight of (a) and (b), of a barrier material.

Preferably, in this third embodiment, the present composition contains:

(a) 1 to 12 wt.%, based on the total weight of (a) and (b), of one or more transfer agents; and

(b) 88 to 99 wt.%, based on the total weight of (a) and (b), of one or more barrier materials.

In a fourth embodiment, the present invention provides a method for cleaning and removing contamination from the skin while forming a protective barrier on skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(a) 0.25 to 25 wt.%, based on the total weight of (a) and (b), of transfer agent; and

(b) 75 to 99.75 wt.%, based on the total weight of (a) and (b), of a barrier material.

Preferably, in this fourth embodiment, the present composition contains:

(a) 1 to 12 wt.%, based on the total weight of (a) and (b), of one or more transfer agents; and

(b) 88 to 99 wt.%, based on the total weight of (a) and (b), one or more barrier materials.

In a fifth embodiment, the present invention provides a method for applying a skin care agent to skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(a′) 65 to 99.75 wt.%, based on the total weight of (a′) and (b′), of one or more barrier materials; and

(b′) 0.25 to 35 wt.%, based on the total weight of (a′) and (b′), of a mixture, said mixture comprising:

(b″) 0.25 to 99.99 wt.%, based on the total weight of (b″) and (b‴), of one or more transfer agents; and

(b‴) 0.01 to 99.75 wt.%, based on the total weight of (b″) and (b‴), of at least one skin care agent,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition.

Preferably, in this fifth embodiment, the present composition contains:

(a′) 75 to 99 wt.%, based on the total weight of (a′) and (b′), of one or more barrier materials; and

(b′) 1 to 25 wt.%, based on the total weight of (a′) and (b′), of a mixture, said mixture comprising:

(b″) 1 to 99.9 wt.%, based on the total weight of (b″) and (b‴), of one or more transfer agents; and

(b‴) 0.1 to 99 wt.%, based on the total weight of (b″) and (b‴), of one or more skin care active agents,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition.

In a sixth embodiment, the present invention provides a method for applying a skin care agent to the skin, which comprises applying to the skin a composition, said composition comprising:

(A) 5 to 90 wt.%, based on the total weight of (A) and (B), of one or more compositions described in the first or second embodiments; and

(B) 10 to 95 wt.%, based on the total weight of (A) and (B), of one or more volatile diluents compatible with the other ingredients of the composition.

In a seventh embodiment, the present invention provides novel compositions which comprise:

(1) 25 to 80 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 1 to 50 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 20 to 50 wt.%, based on the total weight of (1), (2), and (3), of water.

Preferably, in this seventh embodiment, the present composition contains:

(1) 30 to 60 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 10 to 40 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 30 to 40 wt.%, based on the total weight of (1), (2), and (3), of water.

In an eighth embodiment, the present invention provides a method for applying a skin care agent to skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(1) 25 to 80 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 1 to 50 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 20 to 50 wt.%, based on the total weight of (1), (2), and (3), of water.

Preferably, in this eighth embodiment, the present composition contains:

(1) 30 to 60 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 10 to 40 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 30 to 40 wt.%, based on the total weight of (1), (2), and (3), of water.

In an ninth embodiment, the present invention provides novel compositions which comprise:

(i) 1 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 10 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 1 to 50 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan.

Preferably, in this ninth embodiment, the present composition contains:

(i) 5 to 25 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 15 to 25 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 10 to 40 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan.

In a tenth embodiment, the present invention provides a method for applying a skin care agent to skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(i) 1 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 10 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 1 to 50 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan.

Preferably, in this tenth embodiment, the present composition comprises:

(i) 5 to 25 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 15 to 25 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 10 to 40 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan.

THE TRANSFER AGENT FUNCTION

To adhere a hydrophobic barrier material to the skin, especially to wet skin or skin immersed in water, a bi-functional transfer agent material is employed. This material has some active groups which are electrostatically positively charged and some groups which are compatible with the hydrophobic materials of the barrier.

Useful transfer agent materials include various cetyl amine compounds, various diamines (including for example, Duomeens and Ethoduomeens), nitroparaffin-derived heterocyclic amines, quaternary ammonium compounds, and the like. Also useful are compounds of certain cationic polyelectrolytes, including, for example, polyethyleneimine (PEI) derivatized with varying concentrations of fatty acids such as, for example, stearic acid, palmitic acid, oleic acid, etc.

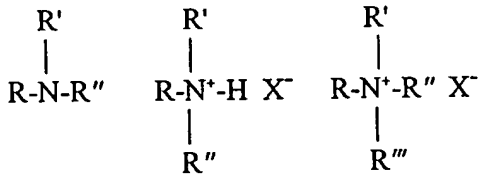
Suitable transfer agents are disclosed in U.S. Patent Nos. 5,665,333, 5,888,480, 5,980,868, and 5,961,958 all of which are incorporated herein by reference in their entirety.

Transfer Agent Materials:

Cationic transfer agent materials useful in the present invention are believed to attach to the skin via an electrostatic interaction between the cationic portion of the material and the negatively charged portion of the skin and thus predispose or

condition the surface of the skin so that a waxy, hydrophobic material will then adhere to the surface. Transfer agent materials that are capable of strong electrostatic bonding to the negatively charged and hydrophilic surfaces of skin include various straight-chain alkylammonium compounds, cyclic alkylammonium compounds, petroleum derived cationics, lecithins, and the like.

a) Straight-chain alkylammonium compounds



R represents a long (C_{8-20}) alkyl chain which may be substituted with one or more hydroxy groups, R', R", and R"' each independently may be either a long (C_{8-20}) alkyl chain which may be substituted with one or more hydroxy groups or a smaller (C_{1-4}) alkyl groups which may be substituted with one or more hydroxy groups or aryl (C_{6-10}) groups or hydrogen, and X^- represents an anion such as chloride or fluoride. These schematic formulas are given for the purpose of defining the classes of compounds and represent the simplest concepts of cationic transfer agents whereby one or more hydrophobic alkyl groups are linked to a cationic nitrogen atom. In many instances the linkage is more complex as, for example, in $RCONHCH_2CH_2CH_2N(CH_3)_2$. In addition, cationic transfer agents may contain more than one cationic nitrogen atom such as the following class of compounds $RNHCH_2CH_2CH_2NH_2$ and derivatives thereof.

Representative examples of compounds according to the above formulas are:

cetyl trimethylammonium bromide (CTAB),

hexadecyltrimethylammonium bromide (HDTAB),

stearyl dimethylbenzylammonium chloride,

lauryl dimethylbenzylammonium chloride,

cetyl dimethylethylammonium halide,

cetyl dimethylbenzylammonium halide,

cetyl trimethylammonium halide (bromide, chloride, fluoride),

dodecyl ethyldimethylammonium halide,

lauryl trimethylammonium halide,

coconut alkyltrimethylammonium halide,

N,N-C_{8-20}-dialkyldimethylammonium halide, and specifically compounds such as bis(hydrogenated tallow alkyl) dimethylammonium chloride which is known to adsorb onto the surface with hydrophobic groups oriented away from it, 2-hydroxydodecyl-2-hydroxyethyl dimethyl ammonium chloride and N-octadecyl-N,N',N'-tris-(2-hydroxyethyl)-1,3-diaminopropane dihydrofluoride.

b) Cyclic Alkylammonium Compounds

A further preferred group of compounds of the present invention which have been found to be applicable includes a class of surface-active quaternary ammonium compounds in which the nitrogen atom carrying the cationic charge is part of a heterocyclic ring. Suitable compounds, for example, are as follows:

laurylpyridinium chloride or bromide,

tetradecylpyridinium bromide,

cetylpyridinium halide (chloride, bromide or fluoride).

5-amino-1,3-bis(2-ethylhexyl)-5-methylhexahydro-5-methylpyrimidine (hexetidine)

c) Petroleum Derived Cationics

Typical basic amines are derived from petroleum-based raw materials such as olefins, paraffins, and aromatic hydrocarbons and include compounds with at least one aliphatic carbon chain containing six or more carbon atoms attached to the nitrogen. Thus, amine salts, diamines, amidoamines, alkoxylated amines, and their respective quaternary salts are applicable.

Preferred compounds of this type include tallow or coco alkyl substituted 1,3-propylene diamines sold by Witco under the trade names of "Adogen" and "Emcol" and similar diamines sold by Akzo under the trade name "Duomeen" and their polyethenoxy derivatives under the trade names of "Ethomeen" and "Ethoduomeens".

d) Polymeric Amines

Suitable polymeric amines comprise a class of polymers containing ionic groups along the backbone chain and exhibit properties of both electrolytes and polymers. These materials contain nitrogen, of primary, secondary, tertiary or quaternary functionality in their backbone and may have weight average molecular weights as low as about 100 or higher than about 100,000. Representative of these polymeric cationic transfer agents are the following:

polydimeryl polyamine (General Mills Chemical Co.),

polyamide (trade name "Versamide"),

polyacrylamides,

polydiallyldimethylammonium chloride ("Cat-Floc"), polyhexamethylene biguanide compounds as sold under the trade name "Vantocil", and also other biguanides, for example those disclosed in U.S. Patent Nos. 2,684,924, 2,990,425, 3,183,230, 3,468,898, 4,022,834, 4,053,636 and 4,198,425,

1,5-dimethyl-1,5-diazaundecamethylene polymethobromide ("Polybrene" from Aldrich),

polyvinylpyrrolidone and their derivatives,

polypeptides,

poly(allylamine) hydrochloride,

polyoxyethylenated amines, and specifically,

polyethyleneimine ("Polymin" from BASF),

and a class of related and surface active cationic polymers prepared by converting a fraction of the amino groups to their acyl derivatives. The polyethyleneimine is first condensed with less than the stoichiometric quantity of acid halides thus alkylating some of the amino groups and the remaining amino groups are then condensed with hydrogen halides such as hydrogen chloride or, preferentially, hydrogen fluoride. The surface activity of these compounds vary with the number of amino groups which are acylated, and with the chain length of the acylating group RCO-. The condensation reaction is typically performed with stearic or oleic acid chlorides in the presence of a solvent containing metal fluoride, preferentially silver fluoride, in such a manner that silver chloride formed in the reaction precipitates from the solvent, as described in

Example XV of U.S. Patent No. 5,665,333, which is incorporated herein by reference in its entirety.

Also suitable, for the purpose of this invention, are cationic derivatives of polysaccharides such as dextran, starch or cellulose, for example, diethylaminoethyl cellulose ("DEAE-cellulose"). Examples of applicable copolymers based on acrylamide and a cationic monomer are available commercially under the trade name RETEN from Hercules Inc., or under the name FLOC AID from National Adhesives. Particular examples of such polymers are FLOC AID 305 and RETEN 220. Similarly useful are acrylamide-based polyelectrolytes as sold by Allied Colloids under the trade name PERCOL. Further examples of suitable materials are the cationic guar derivatives such as those sold under the trade name JAGUAR by Celanese-Hall.

A further preferred group of compounds which comprises a class of water-insoluble polymers, having nitrogen atoms in their molecules, are quaternary polymers of quaternary ammonium type, betaine type, pyridylpyridinium type or vinylpyridinium type. Examples are as follows;

poly(vinyl-benzylmethyllaurylammonium chloride),

poly(vinyl-benzylstearylbetaine),

poly(vinyl-benzyllaurylpyridylpyridinium chloride),

poly(vinyl-benzylcetylammonylhexyl ether) and

quaternized polyoxyethyleneated long chain amines, with the general formula $RN(CH_3)[(C_2H_4O)_xH]_2(+)$ A(-), where A(-) is generally chloride or fluoride, x is a number from 1 to 20, and R is C_{8-22}-alkyl.

These cationic materials, by reacting with the surface of the skin, produce strongly hydrophobic films onto which hydrophobic barrier materials are easily transferred by brushing, rubbing, smearing, or burnishing.

It is important that the reason for this transferability be understood. The surface of human skin is normally hydrophilic and negatively charged. The transfer and adhesion of the barrier materials onto such surfaces is difficult or practically impossible unless the surface is modified by a material that is hydrophobic and therefore compatible with the barrier materials.

In a preferred embodiment, the transfer agent, a cationic surfactant, is a polymer which contains a nitrogen atom in a repeating unit and in which a portion of the nitrogen atoms are quaternized by formation of a salt with a C_{8-20} fatty acid, preferably a C_{12-20} fatty acid. Examples of such polymeric cationic surfactants include polyacrylamides, polyvinylpyridines, or polyamines, e.g., poly(ethyleneimine), in which from 5 to 95 mole%, preferably 40 to 60 mole%, of the nitrogen atoms have been quaternized by formation of a salt with a fatty acid. Typically such polymers will have a weight average molecular weight of 600 to 60,000, preferably 600 to 1,800.

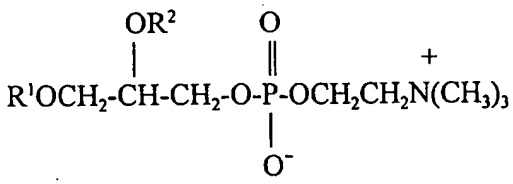
In a another embodiment, the transfer agent is a polymer which contains a nitrogen atom in a repeating unit and in which a first portion of the nitrogen atoms are quaternized with a C_{8-20} fatty acid, preferably a C_{12-20} fatty acid, and a second portion of the nitrogen atoms are quaternized by forming a salt with various acids such as hydrofluoric acid, etc. Examples of such polymeric cationic surfactants include polyacrylamides, polyvinylpyridines or polyamines, e.g., poly(ethyleneimine), in

which from 5 to 95 mole%, preferably from 40 to 60 mole %, of the nitrogen atoms are converted to their acid derivatives by reaction with stearic or oleic acid chlorides, and from 5 to 95 mole%, preferably from 40 to 60 mole%, of the nitrogen atoms are quaternized with acetic acid. In this case, the polymeric cationic surfactant will have a weight average molecular weight of 600 to 60,000, preferably 600 to 1,800.

In another preferred embodiment, the transfer agent is a C_{8-20}-alkylamine which has been quaternized with citric acid, such as cetylamine citrate.

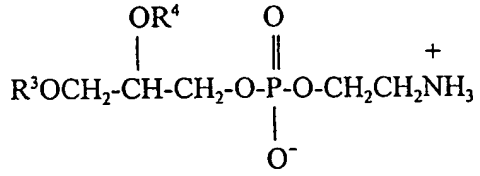
e) Lecithins

In the present context, the term lecithin includes compounds of the formulae (I) and (II)



(I)

and



(II)

in which R^1, R^2, R^3, and R^4 are each, independently of each other, a C_{12-22} saturated or unsaturated alkanoyl group, such as stearoyl, palmitoyl, oleoyl, palmitoleoyl, linoleoyl, linolenoyl, arachidonoyl, etc. Also useful in place of lecithins are lecithin-based compounds such as lyso-lecithins, in which R^2 is replaced by hydrogen. Lecithins are described in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd

Ed., Wiley, New York, vol. 14, pp. 250-269 (1981), which is incorporated herein by reference.

In this embodiment, the lecithin may but does not necessarily function as both the transfer agent and, according to the known art, as a skin care active agent. The Examples given below in which lecithin is used alone, in conjunction with waxy materials, demonstrate a physical protective barrier where lecithin functions as a transfer agent.

The following is a list of specific commercially available compounds which can be used as the transfer agent.

I. Primary Amines:

A. Alkyl Amines:

1.	Armeen TD	CAS 61790-33-8	AKZO
2.	Armeen 18	CAS 124-30-1	AKZO
3.	Armeen HT Flake	CAS 61788-45-2	AKZO
4.	Adogen 172-D Oleoamine	CAS 112-90-3	Witco
5.	Adogen 185 Etheramine (C12-15)	CAS 686-10-26-4	Witco
6.	Hexadecylamine	CAS 143-27-1	Sigma-Aldrich

II. Secondary Amines:

A. Dialkyl Amines:

1. Armeen 2HT CAS 61789-79-5 AKZO

$H_3C(CH_2)_{17}NH(CH_2)_{17}CH_3$

2. Adogen 283 Ditridecylamine Witco

III. Tertiary Amines:

A. Monoalkyl Dimethyl Amines:

1. Adogen 340 (flaked) Trihydrogenated tallow amines Witco

2. Armeen DM 18D CAS 124-28-7 AKZO

B. Dialkyl Monomethyl Amines:

1. Adogen 349 CAS 4088-22-6 Witco

Distearylmethylamine

2. Armeen M2HT CAS 16788-63-4 AKZO

C. Trialkyl Amines:

1. Armeen 316 CAS 28947-77-5 AKZO

Trihexadecylamine

D. Cyclic Amines:

1. Hexetidine 5-amino-1,3-bis(2-ethyl-hexyl)-5-methylhexa-hydropyrimidine Angus Chem. Co.

2. Sanguinarine HCl 13-methyl[1,3]benzodi-oxolo[5,6-c]-1,3-dioxolo[4,5-i]phenanthridium Sigma/Aldrich

IV. Mixed Primary and Secondary Amines:

A. Fatty Diamines:

1. Adogen 570 S CAS 61791-55-7 Witco

Tallow 1,3-propylenediamine

2. Arosurf AA-57 CAS 68607-29-4 Witco

V. Ethoxylated Amines:

1. Ethoduomeen T/13 CAS 61790-85-0 AKZO
2. Ethoduomeen T/20 CAS 61790-85-0 AKZ0
3. Ethoduomeen T/25 CAS 61790-85-0 AKZO
4. Ethomeen 18/12 CAS 10213-78-2 AKZO

VI. Amine Salts:

1. Duomeen TDO CAS 61791-53-5 AKZO
2. Cetylamine Hydrofluoride $H_3C(CH_2)_{15}NH_3^+F^-$ (GABA #297)
3. Armac HT CAS 61790-59-8 AKZO

VII. Polyamines:

A. Di- and Triamines:

1. Duomeen S CAS 61791-67-1 AKZO
2. Duomeen T CAS 61791-55-7 AKZO

$H_2N(CH_2)_{18}NH_2$

VIII. Quaternary Ammonium Salts:

A. Alkyltrimethyl Ammonium Salts:

1. Cetyltrimethyl ammonium bromide CAS 57-09-0

Sigma-Aldrich

2. Arquad T-50 Tallow alkyltrimethyl ammonium bromide

AKZO

B. Dialkyldimethyl Ammonium Salts:

1. Arquad 2HT-75 Bis(hydrogenated Tallow-alkyl)dimethyl

ammonium chloride AKZO

2. Bardac 2280 Didecyldimethyl ammonium chloride Lonza

C. Trialkylmethyl Ammonium Salts:

1. Adogen 316 Tricetylmethyl ammonium halide Witco

2. Adogen 422 Behenyltrimethyl Ammonium chloride Witco

D. Benzylalkyl:

1. Arquad DMHTB-75 Dimethylbenzyl hydrogenat ed tallow ammonium chloride AKZO

2. Barquat MB-80 Alkyldimethylbenzyl ammonium chloride Lonza

IX. Imidazolinium Quats:

1. Varisoft 475 CAS 68122-86-1 Witco

X. Pyridinium Quads:

A. Pyridinium Halides:

1. Cetyl Pyridinium Chloride CAS 6004-24-6

XI. Polyelectrolytes:

A. Polymeric Quats:

1. Cat-Floc DL CAS 26062-79-3 Calgon Polydimethylallylammonium chloride

2. Cat-Floc L CAS 26062-79-3 Calgon Polydimethylallylammonium chloride

3. Cat-Floc T-2 CAS 26062-79-3 Calgon

Polydimethylallyl ammonium chloride

XII. Amphoteric Compounds:

A. Betain Derivatives:

1. Amphosol CG Coco amido betain Stepan

2. Amphosol CA Coco amido betain Stepan

B. Proteins and related compounds with isoelectric points greater than physiologic pH (i.e., those which are positively charged when dissolved in body fluids).

1. Type A Gelatin 200 Proteins Kind-Knox

2. N,N-Di-Methylated Casein Methylated protein

Sigma-Aldrich

3. Armeen Z CAS 68469-05-08 AKZO

N-coco β amidobutyric acid

C. Lecthins

1. Lecithin (from egg yolk) Phosphatidylcholine

Sigma-Aldrich

2. Lecithin (from soy bean) Phosphatidylcholine

Sigma-Aldrich

3. Lecithin (Ultralec) Phosphatidylcholine

Archer Daniels Midland

4. Lecithin (Yelkinol) Phosphatidylcholine

Archer Daniels Midland

5. Natural Egg Yolk Phosphatidylcholine

Source of lecithins: Grocery store

THE BARRIER MATERIAL FUNCTION

Now having a mechanism for adhering a protective, hydrophobic material to the skin, any of several hydrophobic barrier materials may be selected to perform this function. A microcrystalline wax or a high molecular weight polydimethylsiloxane, for example, are barrier materials which provide an adherent, conformal, hydrophobic, continuous, inert, colorless or near-colorless barrier. This hydrophobic waxy or polymeric barrier appears to endure in place and function indefinitely or until it is intentionally removed or sloughed off in the normal process of cellular turnover. Thus, with the transfer and barrier functions performed, extended protection is provided against deleterious activities since the treated skin is coated and protected.

In use, the compositions of the present inventions are sprayed, brushed, or rubbed on the skin, even wet skin or skin immersed in water. Importantly, barrier materials are amorphous materials which shear or cleave easily so that materials which may adhere to the surface of the barrier may be removed easily by the application of moderate shear forces. This same low-shear characteristic moves the barrier materials about, exposing any active agent substances blended into the barrier materials.

Suitable barrier materials are disclosed in U.S. Patent No. 5,665,333 and U.S. Patent 5,980,868, which are incorporated herein by reference in their entirety.

Hydrophobic Barrier Materials

It has been found that various hydrophobic compounds of high molecular weight, solid at body temperature and generally similar to fats and waxes are useful as barrier forming materials. Typically they are long chain hydrocarbons, especially normal paraffins having a chain length of 16 carbons or greater, paraffins with several loci of branching and unsaturation, where the extent of such branching and unsaturation does not lower the solidification point below body temperature, and show essentially no solubility in water or other aqueous materials. The major types of these wax-like materials belong to two basic categories:

I. Natural waxes of animal, vegetable or mineral origin such as beeswax, lanolin, spermaceti, carnauba wax, petroleum waxes including paraffin waxes, microcrystalline petrolatum and microcrystalline wax; and

II. Synthetic materials including ethylenic polymers such as polyethylene glycols ("Carbowax"), polymethylene wax ("Paraflint") and various hydrocarbon types as obtained via Fisher-Tropsch synthesis.

Other suitable materials include silicone-based polymers such as polymethylalkylsiloxanes, polydimethylsiloxanes, poly(perfluoroalkylmethyl siloxanes), poly(methyl-3,3,3-trifluoropropyl siloxanes) and various aromatic (phenyl containing) siloxanes as sold by United Chemical.

Also useful are various fluoropolymers where some or all of the hydrogen is replaced by fluorine, including, among others: polytetrafluoroethylene (PTFE); fluorinated polyethylene-propylene (FEP); perfluoroalkoxy (PFA) polypropylene-polyethylene; polyvinylidene fluoride (PVDF); and polyvinylfluoride (PVF).

THE SKIN CARE ACTIVE AGENT FUNCTION

Experimentation with the technology of the present invention demonstrates that many materials known in the art of skin care to provide medical or cosmetic benefits to the skin may be incorporated into the composition of the present invention to enhance the known benefits of such skin care active agents. Through incorporation of known skin care active agents into compositions of the present invention, the known effects of such materials may be improved, by providing greater concentrations of the active agents to come into contact with the skin, by providing longer or extended contact of the active agent with the skin, by preventing removal of the active skin care agents by sweating, washing, swimming, or incidental contact, or by providing for more effective and efficient application of active skin care agents to wet skin, even to skin immersed under water.

In addition, some of the skin care agents tested and described in the Examples below migrated out or diffused away from the areas on which a Protective Coating (PC) was applied so that, to some extent, the skin care function extended to areas not reached by the PC itself. These skin care agents may be blended into the barrier

material so that, as the barrier material is sheared, cleaved, disturbed, eroded, abraded, etc., fresh skin care agent is exposed and freed to function. Alternatively, certain undesirable or "side" effects of some skin care active agents, such as, for example, irritation, may be mitigated by incorporating the skin care active agent into the present invention, thus providing improved tolerance of the patient to the active agent.

Such skin care active agents include, but are not limited to,

Acetic Acid

Aclometasone Dipropionate

Acyclovir

Alclometasone Dipropionate

Aluminum Chlorhydrate

Aluminum Chlorhydroxide

Aluminum Chloride Hexahydrate

Amcinonide

Aminobenzoate Potassium

Ammonium Lactate

Ammonium Mercury

Amphotericin B

Anthralin

Antimicrobial Agents

Bacitracin

Balsam Peru

Benzocaine

Benzoin Compoundecylenate

Benzoyl Peroxide (BPO)

Beta-Carotene

Betamethasone Acetate

Betamethasone Dipropionate

Betamethasone Sodium Phosphate

Betamethasone Valerate

Butaconazole Nitrate

Butamben Picrate

Canthardin

Carbol Fuchsin

Castor Oil

Cetylpyridinium Chloride

Chloramphenicol

Chlorcyclizine

Chlorhexidine

Chlorhexidine Acetate

Chlorhexidine Gluconate

Chloroxine

Chloroxynol

Ciclopirox Olamine

Clindamycin HCl

Clioquinol

Clobetasol Propionate

Clocortolone Pivalate

Clotrimazole

Coal Tar

Collagenase

Cortisone

Cortisone Acetate

Crotamiton

Cyclopentolate HCl

Dapsone

Desonide

Desoxymetasone

Desoxyribonuclease

Dexamethasone

Dexamethasone Acetate

Dexamethasone Sodium Phosphate

Dibucaine

Dichloroacetic Acid

Dichlorophene

Diflorasone Diacetate

Diperodon

Econazole Nitrate

Ephedrine HCl

Erythromycin

Estradiol

Etretinate

Fibrinolysin

Flucinolone

Flucinolone Acetonide

Fluocinonide

Fluorouracil

Fluradrenolone

Flurandrenolide

Fluticasone Propionate

Formaldehyde

Gentamycin Sulfate

Gramicid

Griseofulvin

Guaifenesin

Halcinonide

Halobetasol Propionate

Haloprogin

Hexachlorophene

Hexetadine

Hyaluronidase

Hydrocodone

Hydrocortisone

Hydrocortisone Acetate

Hydrocortisone Butyrate

Hydrocortisone Sodium Phosphate

Hydrocortisone Sodium Succinate

Hydrocortisone Valerate

Hydroquinone

Hydroxyzine HCl

Hydroxyzine Pamoate

Iodine

Iodochlorhydrocodone

Iodoquinol

Isotretinoin

Ketoconazole

Lactic Acid

Lecithin

Lidocaine Hydrochloride

Lindane

Mafenide Acetate

Meclocycline Sulfosalicylate

Methoxsalen

Methylprednisone

Methylprednisone Acetate

Methylprednisone Sodium Succinate

Metronidazole

Miconazole Nitrate

Minoxidil

Mometasone Furoate

Monobenzone

Mupriocin

Naftifine HCl

Neomycin Sulfate

Nitrofurazone

Nystatin

Octyl Methoxycinnamate

Oxybenzone

Oxyquinoline Sulfate

Papain

para-Aminobenzoic Acid

Permethrin

Phentermine HCl

Podophylum

Polymyxin B Sulfate

Potassium Iodide

Pramoxine HCl

Prednicarbate

Prednisolone Sodium Phosphate

Prednisone

Pseudoephedrine

Pyrogallic Acid

Retinoic Acid

Retinol

Salicylic Acid

Saluminum Acid

Scarlet Red

Selenium Sulfide

Silver Nitrate

Silver Sulfadiazine

Sodium Sulfacetimide

Sodium Thiosulfate

Streptokinase

Sulconazole

Sulconazole Nitrate

Sulfabenzamide

Sulfacetamide

Sulfanilamide

Sulfathiazole

Sulfur

Sunscreen Agents

Sutilains

Terconazole

Tetracaine

Tetracycline

Tretinoin

Triacetin

Triamcinolone

Triamcinolone Acetonide

Triamcinolone Diacetate

Trimeprazine Tartrate

Trioxsalen

Triple Dye

Trypsin

Undecylenic Acid

Urea

Vitamins (all)

Zinc Oxide

Zinc Undecylenate

and other agents known in the art to have medical, cosmetic, bactericidal, or other effects on the skin.

In addition, the present composition may also include coloring materials or fragrances to mask any color or odor of the other ingredients or to provide a more desirable appearance and smell. The fragrance or color may be present in an amount

conventionally used for imparting the desired color or scent, typically 0.01 to 5 wt.%, preferably 0.1 to 1.0 wt.%, based on the total weight of the composition.

The present compositions may also include manufacturing aids, modifiers and thickeners, diluents, solvents, emulsifiers, stabilizers, and ingredients which enhance the aroma, appearance, opacity, color, texture, or any other attribute of the composition.

Thus, the present skin care compositions contain, at minimum, a barrier material, such as wax or other hydrophobic polymer, and at least 0.25 wt.% of a transfer agent, which is a compound having one region which is relatively hydrophobic, such as a hydrocarbon chain, and one portion which is positively charged under use conditions, such as a quaternary nitrogen. Anionic materials such as anionic surfactants can quantitatively neutralize a transfer agent by reacting with the positively charged group. Accordingly, addition of any quantity of an anionic surfactant to the present skin care composition will decrease the activity of the transfer agent, and, if enough anionic agent is present, the transfer agent will no longer function.

Thus, the present skin care compositions preferably contain at least 0.25 wt.% of transfer agent above and beyond the amount of transfer agent which is neutralized by any neutralizing anionic reagent also present in the composition (or, in alternative language, the present skin care compositions contain at least 0.25 wt.% of a transfer agent not including the amount of transfer agent which is neutralized by any neutralizing anionic reagent also present in the composition). More preferably, the present skin care compositions preferably contain at least 1 wt.% of transfer agent

above and beyond the amount of transfer agent which is neutralized by any neutralizing anionic reagent also present in the composition. Most preferably, anionic reagents of any kind should not be included in the present skin care composition unless provision is made to physically separate, for example, by encapsulation, the anionic reagent from the cationic transfer agent.

It should be realized that many anionic reagents contain more than one anionic functional group. In such cases, one mole of the anionic reagent may neutralize more than one mole of the transfer agent, and the amount of transfer agent which will be neutralized by the anionic reagent is calculated by taking into account the number of equivalents of anionic neutralizing groups contained in the anionic reagent.

Similarly, soluble compounds with anionic groups which may, for example, remain on the skin after washing with an anionic detergent, can decrease the effectiveness of the present skin care compositions by neutralizing or partially neutralizing the transfer agent. Ordinarily, however, the amount of soluble anionic reagents remaining on skin after washing and thoroughly rinsing will be so small (100- to 100,000-fold lower than the transfer agent) as to inactivate only a very small percentage of the transfer agent, thus having no material effect of the performance of the present skin care compositions.

In the context of the present invention, such anionic reagents include those compounds which contain anionic functional groups which can be thought of as being obtained by the neutralization of a strong acid, i.e., the neutralization of a sulfonic acid to obtain a sulfonate. Such anionic reagents, of course, include anionic surfactants. Anionic surfactants are disclosed in McCutcheon's; Volume 1:

Emulsifiers and Detergents, North American and International Editions, Pub. by McCutcheon's Division, The Manufacturing Confectioner Publishing Co., Glen Rock, NJ USA, which is incorporated herein by reference.

Particularly important classes of anionic surfactants include: sulfates, sulfonates, oxysulfates, and ether sulfates of fatty acids, fatty acid esters, alcohols, and petroleum derivatives, their salts, their aryl, alkyl, and arylalkyl derivatives, and similar synthetic compounds, including but not limited to members of the following groups:

Compound	Manufacturer*
Avirol series	Henkel
Abex series	Rhone-Poulenc
Barium Petronate series	Witco
Alpha-step	Stepan
Alox series	Alox
Actrasol series	Climax Performance Chemicals
Aristonate series	Pilot Chemical
Astromid series	Alco
Astrowet series	Alco
Arylenes	Huntsman
Avenel S series	PPG

*Manufacturers addressed are listed in McCutcheon's, reference cited above.

Sulfoccinates, including but not limited to members of the following groups:

Aerosol series	Cytec Industries

Carboxylated aryl, alkyl, and arylalkyl alcohols and their derivatives, including but not limited to members of the following groups:

Abex 3594	Rhone Poulenc

Aryl, alkyl, and arylalkyl phosphate esters, their sodium salts, and derivatives, including but not limited to members of the following groups:

Acrilev OJP	Finetex
Alkylene series	Hart Products
Actrafos	Climax
Amphisol series	Givaudan-Roure
Barisol series	Dexter

Fatty acid derivatives of organic acids, including but not limited to members of the following groups:

Amisoft series	Ajinomoto USA

Protein based compounds and their derivatives, including but not limited to members of the following groups:

Aminofoam C	Croda
Atrasein 115	Atramax

Organosilane and organosiloxane sulfates, sulfonates, thiosulfates, and their derivatives, including but not limited to members of the following groups:

Abil S-201	Goldschmidt

The present compositions may be prepared by a method in which the barrier material is first suspended or dissolved in an appropriate solvent (e.g. xylene, toluene,

petroleum ether, methanol, ethanol, methyl ethyl ketone, or where, for example, aqueous dispersions of fluorocarbons are selected as barrier materials, water). The transfer agent(s) and, optionally, skin care agent(s) are then added and the solvent removed by, e.g., evaporation. The present compositions may also be prepared by direct mixing of the barrier material and the other ingredients, either stepwise or all together, at or above the melting point of the barrier material, if the other ingredients are stable or will tolerate for a sufficient time such a temperature.

As noted above, one embodiment of the present invention provides compositions which comprise lecithin. Lecithin is a naturally occurring group of phospholipids that is found in nearly every living cell. The food industry has long recognized lecithin as a lipophilic emulsifier used in products like margarine and chocolate. Lecithin lends itself to specific modification techniques to extend the functionality and physical characteristics of lecithin far beyond their natural variations to include a wider range of functionalities such as dispersion, lubrication, and wetting which also involve enhanced specificity of bonding to oppositely charged surfaces. For example, removing oily components, such as triglycerides and fatty acids, from lecithin a significant enhancement in positively charged components is realized.

Also as noted above, one embodiment of the present invention provides compositions which comprise chitosan. Such compositions provide an effective and practical approach to control skin problems in animals. A combined action of natural products such as chitosan and lecithin permits an effective delivery of a waxy barrier to the animal's skin on a continuous basis. Chitosan is a natural product derived from chitin, a polysaccharide found in the exoskeleton of shellfish like shrimp or crabs. It

possesses many of the same properties as plant fibers, however, unlike plant fibers, it has the ability to bind fat significantly, acting as a "fat storage." Chitosan has been reported to have antibacterial properties and also to inhibit formation of plaque/tooth decay. Chitosan is derived from chitin by removing and refining the acetyl groups through a process called de-acetylation. This process converts the neutral chitin molecules into molecules with a strong positive polarity. This positive polarity attracts the chitosan molecule to negatively charged surfaces by ionic interactions (similarly as a magnet attracts steel). Chitosan is commercially available from, e.g., Aldrich Chemical co. 1001 west St. Paul Ave., Milwaukee, WI 53233. A strong affinity of chitosan for fatty or waxy substances makes it an ideal matrix material to bind and confine the present compositions into a self-cohesive and granular form easily incorporated into skin care formulations. The granular form of the final product is not tacky and is easy to handle.

The present method of application may be carried out by contacting the present composition with the skin to effect transfer of the composition to the skin. In a preferred embodiment, the present compositions are applied to human or animal dermis, epidermis, and/or stratum corneum. The exact means of contacting will depend of course on the nature of the composition and/or applicator. Thus, in the case of an atomizer, spraying will suffice to apply the compositions, while creams may be applied with a swab, brush, puff, or by hand.

Thus, the compositions may be applied to the skin to form a "breathable" barrier which can effectively be applied to wet or dry skin to:

1. Produce cosmetically and medically desirable effects through the barrier function alone, without inclusion of a medicament, cosmetic, or other active ingredient; and

2. Carry known or yet to be discovered medicaments, cosmetic, or other active agents and hold them in contact with the skin in higher concentrations, and/or for extended periods of time, and/or in a more aesthetically desirable condition to provide performance superior to the same ingredients when applied to the skin via conventional vehicles.

Accordingly, the present compositions and methods may be used to prevent, treat, cure and relieve symptoms of diseases and conditions of the skin, internal and external membranes, mucosa, blood, lymphatic and other vessels and glomeruli of the body and its organs including systemic disease and conditions having primary or ancillary signs or symptoms manifesting in or on the skin, internal and external membranes, mucosa, blood, lymphatic and other vessels and glomeruli of the body and its organs, including but not limited to allergies, dermatitises, dermatoses, bacterial, fungal, and parasitic infestations and infections, abrasions, lacerations, cuts, burns, and other insults and injuries resulting from or related to injury or normal or abnormal metabolic, pathologic, or immunological processes. Such diseases and conditions include but are not limited to acne, athlete's foot, jock itch, ringworm, hemorrhoids, nail infections, skin infections, sunburn and sun- or injury-induced pigmentation, psoriasis, seborrhea, eczema and other dermatitises, dermatoses, and other diseases and pathological processes including kidney diseases, atherscleroses,

etc. listed in Dorland's Illustrated Medical Dictionary, Stedman's Medical Dictionary, and other sources.

The present compositions and methods are useful to minimize the appearance of skin imperfections, to help shed dry, damaged cells and unclog pores, to moisturize, exfoliate, and reveal younger-looking skin, to ameliorate and minimize the visible signs of aging, to ameliorate, minimize, and manage complexion problems, to gently peel away outer layers of dry, sun-damaged skin to expose younger looking skin, to leave skin smooth, soft, and refreshed, to ameliorate or minimize cosmetic problems associated with dry, sensitive, normal, combination-oily skin, to help control oily or problem-prone skin, to soothe the skin, improve skin texture, and restore moisture to the skin, to smooth fine lines in the skin, to even skin tones, to refine the texture of the skin, to improve and treat acne-prone skin, to protect against environmental skin aging, to lighten pigmented areas, and to enhance and accelerate the results achieved with other products.

Thus, the present composition may take the form of:

1. Makeup
2. Makeup Foundation
3. Makeup Remover
4. Eye Makeup
5. Eye Makeup Remover
6. Eye Makeup Pencil
7. Eye shadow
8. Facial Cream

9. Facial Cleanser
10. Facial Emulsion
11. Facial Mask
12. Facial Makeup
13. Facial Scrub
14. Hand Cream
15. Body Cream
16. Sun Tan Lotion (including Sun Screen)
17. Lotion
18. Baby Oil
19. Baby Lotion
20. Anti-Aging Cream
21. Night Cream
22. Vanishing Cream
23. Cold Cream
24. Balm
25. Skin Conditioner
26. Disposable Wipe
27. Baby Wipe
28. Cleansing Cream
29. Lip Conditioner
30. Chap Preventative
31. Wound Care Ointment

32. Foundation for Lipstick (when applied to the lips before applying lipstick, the present composition locks or bonds the lipstick in place; no "feathering" or "bleeding" takes place and it looks as good 10 hours after application as it did just following application.)

33. Ingredient in Make-Up (lasts longer and goes on wet)

34. Anti-Perspirant/Deodorant

35. Wound Care (anti-adhesion, anti-infection, may contain antibiotic, *e.g.*, Neosporin, etc.)

36. Surgical Site Wound Care

37. Implants (can provide anti-adhesion, anti-infection benefits when applied to the skin or tissues in contact with implants, *e.g.*, pacemakers, etc. or on certain surfaces of the implant itself. Many conventional pacemaker implants produce infections which require removal and re-implantation. Application of the present composition to the skin or tissues in contact with the implant or on certain surfaces of the implant itself may prevent the adhesion of surrounding tissues to the implant, where desirable and also prevent or decrease the rate of infection, especially when the present composition comprises one or more anti-bacterial agents.)

38. Indwelling Instruments (the present composition may provide anti-adhesion and anti-infection benefits when applied to the skin or tissues in contact with indwelling instruments, *e.g.*, catheters, etc. or on certain surfaces of the indwelling instrument itself.)

39. Surgical Sites, Instruments, Sutures (coating surgical instruments and/or sutures with the present invention may provide anti-adhesion and anti-infection benefits and may reduce the resistance to placing the sutures by reducing the frictional resistance of the sutures.)

40. Athlete's Foot (the present invention even without an active agent may provide benefits; hexetidine is not only a preferred transfer agent but also a good anti-fungal material as well as a weak anti-bacterial material; thus, compositions which contain about 5% by weight hexetidine provide extended contact time with the affected area.)

41. Jock-Itch (jock-itch is caused by the same fungus responsible for athlete's foot and application of the present composition to the affected area may be effective for the prevention and/or treatment of jock-itch.)

42. Anti-Itch (the present compositions may be used as anti-itch compositions, even without inclusion of an active agent, especially when the itching is caused by external stimuli; traditional ani-itch agents, *e.g.*, hydrocortizone may also be included in the present compositions.)

43. Diaper Rash (the present compositions may be applied to the affected area or to the diaper itself to combat diaper rash.)

44. Anti-Wrinkle Products (the present composition may be used to reduce wrinkles even without the presence of an active agent; alternatively, the present composition may contain an anti-wrinkle active agent such as shark liver oil.)

45. Anti-Anal Itch (the present composition may be applied to the affected area to combat anal itch even without an added active agent; traditional ani-itch agents, *e.g.*, hydrocortizone may also be included in the present compositions; the ability of the present compositions to adhere to moist surfaces means that it will stay in place longer and require fewer applications.)

46. Muscle Rub (compositions according to the present invention which contain a circulation-stimulating active agent, *e.g.*, capsicum, etc. may be applied to the skin to treat sore or stiff muscles; the adherence of the present compositions to the skin means that the circulation-stimulating active agent (and resultant heat) will remain in contact with the affected area longer.)

47. Poison Oak, Ivy, Sumac, Etc. (the present compositions may be applied to the skin prior to engaging in activity which would bring the skin into contact with poisonous plants, e.g., poison ivy, poison oak, poison sumac, etc. and serve as a prophylactic barrier even without an active agent; the present compositions may also be applied to skin already suffering from poison ivy, poison oak, poison sumac, etc. to reduce the itching and spread of the condition with or without an anti-itching active agent.)

48. Depilatory Enhancer (hair absorbs moisture and is then more easily cut and/or removed; application of the present composition allows the depilatory to be applied when the hair is wet, thereby enhancing the cutting and/or removal of the hair.)

49. Anti-Drying (the present compositions may be used to form a protective barrier on the skin to prevent loss of moisture and/or oils from the skin.)

50. Other forms which will be apparent to those skilled in the art.

It should be understood that in the above-listed applications, the present composition may comprise either: (1) a transfer agent and a barrier material; or (2) a transfer agent, barrier material, and active agent. In other words, for the applications listed above, good effects may be achieved even without the addition of an active agent, but in certain situations it may be advantageous and/or desirable to add an active agent.

The present compositions are typically applied to the skin in an amount effective to provide a protective barrier on the skin, usually about 80 micrograms to about 0.5 grams per cm^2 of skin, preferably 100 micrograms to 0.1 grams per cm^2 of skin.

Although the present invention has been described in detail in the context of skin care compositions and methods for treating the skin, the present compositions may be applied to substrates other than skin and may be used in methods other than skin care. In particular, it should be understood that the present compositions may be used in the following non-skin care applications.

1. Mold releases and casting adhesives. The release of a cast article from a mold may be enhanced by application of the present composition to the interior surface of the mold, or to the object to be cast or molded. This method may be especially effective for enhancing the release of a cast article made from a hydrophilic material (certain plastics and ceramics) from a mold which has a hydrophilic interior surface.

2. Ink and dye processing. The present compositions may be used to enhance the adherence of a hydrophobic ink to a hydrophilic substrate or vice-versa. In particular, the hydrophilic substrate may be coated with the present composition either over the entire surface or in a patternwise fashion. Application of the present composition to a hydrophilic surface may also be used to advantage in batik and tie-dye processes.

3. Anti-fouling applications. In marine applications, the present compositions may be applied to surfaces subject to fouling without hauling-out due to the ability of the present compositions to be applied to wet surfaces. The present compositions are useful as anti-fouling agents with or without active agents such as antibacterial agents. This is an important advantage, since most of the traditional anti-fouling materials, *e.g.*, tin, copper, etc., are toxic to some marine organisms. When coated on a ship's hull, the present compositions may inhibit the attachment of marine growth to the hull or reduce the adherence of marine growth to the hull such that moving through the water at a speed of a few knots may be sufficient to remove any marine growth. In addition, the turbine blades of hydroelectric generators are plagued with fouling. Application of the present composition may be effective for reducing the fouling of turbine blades even in the face of the large shear forces encountered by turbine blades.

4. Leather treatments. Oils are destructive to leathers; they soften them and allow them to stretch and/or crack and they provide an attachment for grit and abrasives. Waxes are the preferred protectants. However, waxes applied

directly to leathers are easily removed. Application of the present composition to leather provides extended benefits and reduced drying. In addition, since the outer layers slough off, less dirt will adhere to the leather.

5. Auto, vehicle protection. Application of the present composition to the interior and exterior surfaces of automobiles and other vehicles may be effective for protecting and/or enhancing the appearance and endurance or longevity of those surfaces. This may be especially effective for protecting hydrophilic surfaces such as certain seat coverings or other materials.

6. Wood protectant. Wood is negatively charged on the surface and contains moisture. The present compositions may thus be used as a furniture polish with excellent results, especially when rubbed down to a very thin but protective hydrophobic layer. The present compositions prevent water damage, *e.g.*, water rings and stains. The present compositions may also be used to prevent wood from swelling, as in wood casement windows, and protect against mildew.

7. Metal treatments. The present compositions may be applied to metals to protect against oxidation, staining, chemical attack, and tarnishing.

8. Ceramic sealant. The present composition may be applied to certain ceramics to prevent and/or reduce the staining or fouling of the ceramic. For example, the present composition may be applied to showers, bathtubs, ceramic tile, and grout to prevent the formation of mold and mildew stains and bathtub rings.

9. Painted surfaces. The present composition may be applied to painted surfaces to afford a protective surface.

10. Floor wax. The present composition may be used as a floor wax, especially on floors with a hydrophilic surface, such as wood floors.

11. Anti-graffiti coatings. The present composition may be applied to surfaces which are subject to graffiti attacks, such as buildings, billboards, train cars, etc. The hydrophobic barrier afforded by the present composition not only makes it more difficult to apply the graffiti in the first place but also makes it easier to remove graffiti which is applied.

12. Paper and cardboard coatings. The present composition may be applied to paper or cardboard to obtain a moisture resistant barrier. This application may be useful not only for protecting the contents of a paper or cardboard package from water or moisture damage, but also for preparing a paper or cardboard package suitable for storing liquids such as milk or juice.

13. Plastics and fiberglass. The present composition may be applied to plastics or fiberglass to protect, lubricate, seal, or waterproof the plastic or fiberglass.

14. Anti-stick coatings. The present coatings may be applied to the cooking surfaces of cooking utensils, pots, pans, etc. as an anti-sticking agent. In such applications, it may be desirable to formulate the present composition with a volatile propellant and to apply the composition by means of an aerosol can.

15. Glass or china protectant. The present composition may be applied to glass or china to form a protective barrier which will keep the surface cleaner.

16. Pesticides. The present composition may be formulated with an active agent which is a pesticide and applied to any surface which is susceptible to infestation by pests. In a preferred embodiment, the present composition

which contains the pesticide may be applied directly to the leaves or foliage of a plant.

17. Anti-fogging, anti-condensation agent. The present composition may be applied to surfaces which are susceptible to fogging, e.g., bathroom mirrors, windshields, eyeglasses, etc.

18. Adhering lubricants to substrates. Application of the present composition to the surface of a substrate is useful for adhering a lubricant such as a wax, grease, petrolatum, teflon, or silicone to the surface of the substrate. In certain situations, it may be preferred or necessary to pretreat the surface of the substrate so that the present composition will itself adhere to the substrate.

The present compositions and methods provide a number of advantages which are not achieved by conventional compositions. In particular, the present compositions are characterized by the following advantages:

1. The present compositions are easily applied to a wet substrate. This advantage is particularly important in the context of skin care as in many circumstances it is desired to apply a skin composition to wet skin.

2. The present compositions bond well to the skin or other substrate resulting in a greater adhesion of the hydrophobic barrier.

3. The present compositions are resistant to removal. Mechanical action is often required to remove them from the skin or other substrate, since the barrier is not easily removed by solubility in aqueous, alcohol or other common personal care systems, but only by organic solvents such as hexane, etc., which are rarely encountered in skin care treatments or compositions.

4. The present compositions extend the time of contact with the skin or other substrate. This is an especially important benefit. Enhanced contact time means enhanced protection afforded by the protective hydrophobic barrier and longer contact time with any active agent present.

5. Enhanced activity of the active agent. The extended contact time exhibited by the present compositions may result in intensifying the benefits of any active agent present in the composition according to the present invention.

6. The present compositions provide a moisture barrier in both directions. In other words, the present compositions are able to keep moisture from escaping from the skin and are thus useful as moisturizers. In addition, the present compositions are also effective for keeping excessive moisture away from the skin and are thus useful for treating conditions related to contact of excess moisture with the skin, *e.g.*, athlete's foot.

7. The present compositions are effective even without the addition of an active agent. In many cases, e.g., anti-perspirants, the combination of the transfer agent and the barrier material alone may provide the desired benefits even without the addition of an active agent. This is an important advantage. The barrier materials in many cases do not inhibit epidermal transpiration. Thus, the present compositions form a "breathable" protective coating. This coating may deny access to the skin or other substrate by bacteria, moisture, acids, and other toxic or contaminating substances.

Permeability/Porosity/Discontinuity:

The 'porosity', in the general or non-technical use of that word, or, more specifically, the permeability or continuity of the barriers formed by the compositions of the present invention, may be controlled by selection of viscosity modifiers, their molecular weights and their concentrations in the formulations of the compositions of the present invention. In general, higher molecular weight materials increase cohesion between the molecules of the barrier materials and reduce the permeability or 'porosity' of the resulting composition when applied.

In addition, transfer agents vary in the extent to which they diffuse through the barrier material selected, so that some transfer agents, such as hexetidine, having a high mobility or diffusability in microcrystalline wax barriers, will demonstrate a high degree of permeability in the barriers formed by the compositions of the present invention and may carry with it other ingredients, such as certain of the active agents, providing permeability of the active agent both to the substrate and to the surfaces presented to the outer environment.

Characteristics of the substrate may also affect the observed permeability of the barriers formed by the compositions of the present invention in application.

Selecting very low molecular weight barrier materials may result in a very thin coating of as little as a single molecular layer of transfer agent combined with a single molecular layer of the barrier material with the functional continuity or porosity of the composition then more importantly dependent upon the characteristics of the substrate to which it is applied.

Specifically, it is possible to vary the permeability of the barrier to various substrates by varying the composition and/or concentrations of the barrier material, the transfer agent, viscosity modifiers, and active agents either independently or proportionately with respect to each other. In addition, the permeability of the barrier formed by the composition of the present invention will necessarily vary with respect to the specific permeant and with the environment in which it exists, e.g., the solubility of the transfer agent in the environment of the surfaces of the barrier formed by the composition of the present invention not in contact with the substrate.

Surface Energy (including Surface Tension/Critical Surface Tension/Interfacial Tension):

In many applications, the surface energy (SE) of the barrier formed by the composition of the present invention will have important implications in functionality. For example, during experimentation and testing of barriers formed by the compositions of the present invention on dental surfaces, it was found that *S. mutans*, an important organism in oral care pathogenicity, will not attach to surfaces having an SE below a certain level. However when the SE is too low, the product can become aesthetically undesirable since the tongue cannot wet the surface of the barriers formed by the compositions of the present invention and the patient or user of the product is repeatedly frustrated in trying to do so. Thus a specific range of SEs is important in this application.

There are several factors which, independently and in combinations among them, may alter or affect the SE of the resulting barriers formed by the compositions of the present invention. Among them are:

1. Selection of the transfer agent(s)

2. Concentration of the transfer agent(s)

3. Solubility of the transfer agent(s) in the environment at the interface of the barrier formed by the composition of the present invention.

4. Selection of the barrier material(s)

5. The rate of permeability/mobility/diffusability of the transfer agent(s) through the barrier formed by the composition of the present invention (for example as a function of the rate and extent to which the transfer agent(s) are replenished at the environmental interface as outer layers of the barrier formed by the composition of the present invention are removed); and that rate with respect to the rate of mobility of active agents through the materix of the barrier formed by the composition of the present invention, etc.

6. Characteristics of the environment, such as pH, etc.

Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

EXAMPLES

In the following examples, and throughout this specification, all parts and percentages are by weight, and all temperatures are in degrees Celsius, unless

expressly stated to be otherwise. Where the solids content of a dispersion or solution is reported, it expresses the weight of solids based on the total weight of the dispersion or solution, respectively. Where a molecular weight is specified, it is the molecular weight range ascribed to the product by the commercial supplier, which is identified. Generally this is believed to be weight average molecular weight.

I. Methods.

A. The Wet Slide Test for Adherence:

The primary functional difference between the compositions of the present invention and compositions which contain barrier materials alone without a transfer agent is that the compositions of the present invention will adhere to a wet negatively-charged surface, such as a wet glass microscope slide but unmodified barrier materials will not adhere. Therefore, the primary functionality test for compositions of the present invention formulations is the Wet Slide Test, Protocol CB 01, which may be used both for initial evaluations of compositions of the present invention and for stability evaluations.

1. Materials

a. Substrate

Glass microscope slides, such as VWR Cat No 48312-400, approximate dimensions 1" x 3" x 1.0 mm, are cleaned (even if "pre-cleaned" slides are purchased) by manually washing for 30 seconds per slide in 2% aqueous sodium lauryl sulfate (90% or greater) solution or equivalent, exhaustively rinsing in tap water, followed by a final rinse in distilled or deionized water, and air drying at room temperature.

b. Water

Water for final rinse of substrate (above) and for test is Alhambra (brand) Distilled Drinking Water (McKesson Water Products Co., Pasadena, CA, 91107 U.S.A) or equivalent.

c. Applicator

Applicator is Longs (brand) Double-Tipped Cotton Swabs (Longs Drug Stores, Walnut Creek, CA 94596 U.S.A.) or equivalent.

d. Control

Hanson Microcrystalline Wax, Hansonwax code JH 835, Dilco Refining Division, Eastern Mohair and Trading Company, Inc. 73-35 Grand Avenue, Maspeth, New York 11378 U.S.A.

2. Procedure

1. The ambient temperature, the temperature of the water, the slide, and the test product must be 25±5°C.

2. Thoroughly coat the applicator tip with Control by rubbing the applicator on and in the Control product.

3. Holding the substrate (slide) horizontal, cover the upper surface of the substrate with water.

4. Wet the applicator and apply the Control to the water-covered surface of the substrate by rubbing the Control-coated tip of the applicator thereon.

5. If the Control transfers (visual assay) to the slide leaving a hydrophobic (high contact angle) area on the substrate, then the slide has been improperly cleaned

(see Substrate, above). In such case, the whole batch of cleaned slides (Substrate) should be re-cleaned as provided under Methods (Substrate).

6. If the Control does not produce a hydrophobic area, then test a Test Product as in steps 1-4 (Procedure) above.

3. Evaluations

Evaluation of performance is by a visual assay. First, observe a substrate which is covered with water. Note visually the magnitude of the contact angle between water and the surface (not an edge) of the substrate. Test materials which are judged to be effective (a report of +, ++, or +++) will produce a contact angle with water greater than that produced by water in contact with a cleaned substrate. Test materials which are ineffective (a report of -) will not deposit material on the substrate in the test and will not produce an increased contact angle between water and treated surface.

4. Functionality

\- Describes the performance of Control or an ineffective test product. No test material is deposited on the surface of the substrate (slide) in the test and the contact angle between water and the substrate is not changed as compared to the water-coated substrate prior to test.

\+ Describes the performance of a marginally effective product. A small amount of test material is discontinuously deposited on the substrate (slide) in the test and the contact angle is little increased as compared to the water-coated substrate prior to test.

++ Describes a product of intermediate effectiveness. An intermediate amount of test material is deposited on the substrate (slide) in the test and the contact angle is somewhat increased as compared to the water-coated substrate prior to test.

+++ Describes a highly effective test material. A substantial amount of test material is continuously deposited on the substrate (slide) in the test and the contact angle is greatly increased as compared to the water-coated substrate prior to test.

II. Examples:

Example 1.

Polydimethylsiloxanes (PMDS) of various molecular weights, obtained from United Chemical Technologies, Inc. (UCT), were mixed, using a spatula, with a transfer agent, hexetidine, in a ratio of 0.1 milliliter of transfer agent (abbreviated Hx) to 2.0 g of polymer or polymer mixture. Mixtures of polymers are in a ratio of 4 g of the higher MW polymer plus 1 g of the lower MW polymer. The higher molecular weight polymers required substantial time and force to produce a homogeneous mixture. Each of the mixtures described below was then tested in the wet slide test as indicated below:

Polydimethylsiloxanes:

Cat.No.	Viscosity (cs)	MW	Hazard
P-034	0.65	162	Irritant
P-040	50	3,780	None

P-042	500	17,250	None
P-044	5000	49,350	None
P-048	100,000	139,000	None
P-049	600,000	260,000	None
P-049.5	1,000,000	308,000	None
P-050	2,500,000	423,000	None

Make the following formulations:

No.	Composition	Wet Slide Test
1.	P-034	-
2.	P-034, Hx	++
3.	P-040	-
4.	P-040, Hx	+++
5.	P-042	-
6.	P-042, Hx	+++
7.	P-044	-
8.	P-044, Hx	+++
9.	P-048	-
10.	P-048, Hx	+++
11.	P-048, P-034, Hx	+++
12.	P-48, P-040, Hx	+++
13.	P-048, P-042, Hx	+++
14.	P-049	-

15.	P-049, Hx	+++
16.	P-049, P-034, Hx	+++
17.	P-049, P-040, Hx	+++
18.	P-049, P-042, Hx	+++
19.	P-049.5	-
20.	P-049.5, Hx	+++
21.	P-049.5, P-034, Hx	+++
22.	P-049.5, P-040, Hx	+++
23.	P-049.5, P-042, Hx	+++
24.	P-050	-
25.	P-050, Hx	+++

Example 2.

100 Grams of UCT PS050 polydimethylsiloxane, approximately 2,500,000 centistokes viscosity was mixed with 6.0 g of hexetidine. Clove oil (0.2 milliliter) was added for aroma and approximately 200 g of octamethylcyclotetrasiloxane (GE 1173) was added to decrease viscosity and allow thorough mixing. The formulation was tested as a protective hand and face preparation; users reported good effects. It was noted that the preparation could be applied to wet skin to moisturize and seal in moisture. Similar formulations having between half as much volatile silicone diluent to twice as much volatile silicone diluent had similar attributes but the more dilute formulations left a thinner coating of silicone on the skin.

Example 3.

75 Grams of wax was melted at approximately 85 °C and 3.8 g of hexetidine was added. Then the mixture was diluted with approximately 150 g of SF 1173 (General Electric octamethylcyclotetrasiloxane). This formulation was tested as is in the wet slide test (results positive) and as a makeup foundation. It was also further diluted with up to 450 more grams of volatile silicone diluent. All dilutions gave similar results, some subjects preferring the less viscous formulations and some preferring the more viscous formulations. This formulation had exceptional performance in minimizing imperfections in the skin, especially when used as a make up foundation. In this mode of use, the skin is first washed thoroughly and then the makeup foundation preparation is applied liberally to sparingly all over the face. It is notable that, even when applying the preparation to skin blemishes and lesions which are oozing tissue fluids, the preparation goes on easily and evenly, adhering uniformly to damaged and undamaged regions alike. After allowing a few moments for the foundation to dry, ordinary facial make up is applied in the usual manner. It is notable that when this formulation is applied to the skin as a foundation, ordinary makeup, which can often accentuate rather than hide oozing and dry skin blemishes and lesions, goes evenly and uniformly over healthy and blemished skin alike, evening out skin tones and hiding blemishes very effectively. It is also noted that when make up is removed by washing, this make up foundation preparation aids in cleaning the skin.

Example 4.

The following skin care formulations were prepared by mixing the ingredients under the conditions indicated:

Formulation	Wax	Trans. Agent	Diluent (SF1202)	Wet Slide Test
1	33g	1.0ml	66g	+++
2	49g	1.5ml	50g	+++
3	25g	1.0ml	74g	+++
4	30g	1.0ml	63g	+++
5	6.25g	0.25ml	43.5	+++

Numbers 1, 2, and 3 were prepared by melting the wax at approximately 85 °C, adding hexetidine and diluent, and mixing thoroughly. Number 5 is prepared by heating 25 g of number 3 to melt and diluting with 25 g of diluent, then cooling with stirring. Number 4 is a medicated formulation containing benzoyl peroxide, a recognized anti-acne agent. Benzoyl peroxide (BPO) is obtained from UCT as PC 020-KG, a paste which is 50% BPO in polydimethylsiloxane (PDMS). The BPO paste is first mixed with diluent at approximately 25 °C then warmed to 75 °C in a water bath, while the wax is melted together with hexetidine at approximately 90 °C. Then, the wax mixture is poured into the BPO-diluent mixture stirring on the water bath and the final mixture is cooled while shaking.

Formulations 1, 2, 3, and 5 performed essentially the same as the formulation described in Example 3. Formulation 4 was cosmetically similar to the above

formulations but was effective in one day and even more effective when used daily over two weeks in controlling acne. While BPO is a recognized anti-acne agent, most formulations incorporating this ingredient do not provide desirable cosmetic appearance when in use. Such conventional BPO formulations tend to dry and can often irritate the skin and often can accentuate rather than hide blemishes and tend to result in uneven skin tones, even when conventional make up is applied over a BPO foundation. In contrast, formulation 4 exhibited all the favorable cosmetic attributes and functionalities of the other formulations (1, 2, 3, and 5 as well as Example 3) while treating and ameliorating acne lesions with superior efficacy. In short, the present formulation seems to enhance the activity of BPO, allowing it to work more quickly, to hide blemishes while it is working, and to allow BPO to be used for many days continuously for overall superior results.

Example 5.

In this example, BPO is 50% Benzoyl Peroxide in PDMS, UCT # PCO20-KG, Lot 120715. BPO is a monographed over-the counter (OTC) acne medication which, heretofore, has not been formulated in really esthetic products. This example, in which BPO constitutes 10% of the non-volatile fraction of the product (10% is the OTC limit), is prepared as follows:

Dilute 6.7 g of BPO in 68 g of cyclomethicone (GE SF1202, decamethylcyclopentasiloxane and octamethylcyclotetrasiloxane) and warm to 80 °C with stirring. Melt 25 g of wax and add 1.7 g of hexetidine. Pour the wax mixture into the BPO mixture and stir. Dispense into bottles.

A different order of addition (mix the BPO with the hexetidine, add melted wax, and then add the cyclomethicone) gave the same results.

The final composition is 5% hexetidine, 10% BPO, in the wax (exclusive of volatiles), its performance was the same as for formulation number 4 in Example 4 above.

Example 6.

A waterproof sunscreen is prepared as follows:

Dissolve 15 g of UTC PS 050 (2,500,000 cs PDMS) in 100 g of decamethylcyclotetrasiloxane. Add 5 g of 2-ethylhexyl-trans-methoxy-cinnamate ("Octamethyl Cinnamate," a UV absorber used in sunscreen products) and 1 g of hexetidine and stir. Observation: it doesn't wash off.

Example 7.

This Example is similar to Example 2 which uses PDMS as the barrier and Example 3 which uses wax as the barrier. This example uses a mixture of wax and PDMS as the barrier and is prepared using the following amounts of ingredients and the following procedure:

16.6 g of PS049.5 (1,000,000 cs PDMS)

16.6 g of Wax

1 g of Hexetidene

66.4 g of solvent GE SF1202

Mix the PDMS with the solvent and warm to about 85 °C; add the wax and stir, to melt and mix; add the hexetidine and stir; and shake while cooling.

The formulation is superior to both Examples 2 and 3 in that the ratio of the two distinctly different barrier materials may be varied to produce cosmetic preparations which deliver a range of skin feel from relatively "hard," with a preponderance of wax, to supple, with a preponderance of PDMS.

Example 8.

Three formulations are prepared as follows:

A) 2% hexetidine.

Melt 83 grams of wax at 90 °C, add 15 grams of oil and 2 grams of hexetidine, and mix by stirring.

B) 6% Lecithin, 1% Hexetidine.

Mix 6 grams of lecithin, 100 ml of hexane, and 15 grams of oil by stirring, then add 1 gram of hexetidine with stirring. Warm just to the boiling point of hexane and gently evaporate the hexane. Add 78 grams of wax and melt at 75°C on a water bath. Mix by stirring.

C) 12% Lecithin

Mix 12 grams of of lecithin, 100 ml of hexane, and 15 grams of oil by stirring. Warm just to the boiling point of hexane and gently evaporate the hexane. Add 73 grams of wax and melt at 75 °C on a water bath. Mix by stirring.

Melt A and C on a water bath. Add 50 grams of A to 50 grams of B, and mix by stirring.

Formula	Barrier (Wax)	Transfer Agent		Viscosity Modifier (oil)	Rating
		Lecithin	Hexetidine		
A	83 g	0 g	2 g	15 g	+++
B	78 g	6 g	1 g	15 g	+++
C	73 g	12 g	0 g	15 g	+++

+++ Highly effective, ++ Effective, + Somewhat Effective, - Ineffective.

The lecithin formulations give an exceptional degree of suppleness, and the lecithin itself may, to some extent, plasticize the skin, this being a natural component of the skin.

Example 9.

A silicone-based skin formulation is prepared using the following amounts of ingredients and the following procedure:

33.0 g of PS 050 (2,500,000 cs PDMS),

132 g of GE Octamethylcyclotetrasiloxane, and

1.0 ml of hexetidine,

Heat no higher than 60°C and stir overnight.

This composition passes the wet slide test.

Example 10.

These silicone formulations are prepared using the following amounts of ingredients and the following procedures:

1. Mix 23.7 g of UCT PS 050 (2,500,000cs PDMS) with

71.1 g of Decamethycyclopentasiloxane (G.E.);

Heat and stir to dissolve (Takes a long time);

Add 1.0 g of hexetidine; and mix well.

Wet glass slide test: +++

2. Melt 40.5 g of Wax, at ca. 85 °C;

Add 4.0 g of Hexetidine, mix well;

Add 40.5 g of Decamethycyclopentasiloxane (G.E.); and

Mix well.

Wet glass slide test: +++

3. Mix 33.2 g of melted formulation no. 2 with

33.2 g of Decamethylcyclopentasiloxane (G.E.);

Mix well.

Wet glass slide test: +++

4.

Controls	Wet glass slide test:
Wax:	-
Decamethycyclopentasiloxane (G.E.)	-
UCT PS 050 (2,500,000cs PDMS)	-

Note that a control formulation, without transfer agent, did not pass the wet slide test.

Example 11.

An athletes foot formulation is prepared using the following amounts of ingredients and the following procedure;

278 g of wax (75%),

55 g of oil (15%), and

37 g of hexetidine (10%) (50 ml of 90% hexetidine).

Heat to melt wax and mix; and

Dispense into containers.

It is reported that this formulation rapidly treats and cures athletes foot (fungal infection).

Wax-Based Cream Formulations:

Example 12.

The wax-based hand-cream formulation was prepared by combining 10 grams of microcrystalline wax, 10 grams of 50% lecithin* dissolved in paraffin oil, 10 grams of water, 2 grams of isopropyl alcohol, 0.5 grams of hexetidine and 1 gram of citronella fragrance (Aura Cacia,** 100% essential oil). The mixture was liquefied by heating to approx. 90°C. It was stirred vigorously until the temperature dropped below 50°C and the mixture solidified into a formulation which is smooth and creamy in consistency. In this type of formulation, the ratio of water and wax may be varied to produce cosmetic preparations which deliver a range of skin feel from relatively "soft," with a preponderance of water, to 'hard," with a preponderance of wax.

Example 13.

The wax-based cream composition, suitable as a base for makeup, was prepared by combining 10 grams of microcrystalline wax with 4 grams of 50% lecithin dissolved in paraffin oil, 2 grams of 50% beeswax dissolved in paraffin oil, 10 grams of water, 0.5 grams of hexetidine, and 1 gram of orange fragrance (Aura Cacia, 100% essential oil). The mixture was liquefied by heating to approx. 90°C. It was stirred vigorously until the temperature dropped below 50°C and the mixture solidified into a smooth creamy consistency suitable for mascaras and eye makeup.

Wax	25% to 80%
Lecithin	1% to 50%
Water	25% to 50%

* Manufactured by Archer Daniel Midload Co. under trade name of ULTRALEC P, lot# UF/040

** Manufactured by Aura Cacia, Weaverville, Ca.

Chitosan-Containing Composition:

Example 14.

A composition including de-oiled lecithin is shown in the table below:

Components	Weight %
Microcrystalline Wax	70
Paraffine Oil	25
Liquid Lecithin	5

In a typical product preparation, 10 grams of the above formulation is liquefied by heating to 80-100°C and combined with 10 grams of de-acetylated chitosan (Aldrich Chemical Co., 1001 West St. Paul Ave., Milwaukee, WI 53233, catalog no. 44,887-7). The components are mixed until a homogenous paste is obtained. In a separate container, 100 ml of water containing one g of a chitosan fiber dispersion is heated to 80°C and maintained at this temperature. The lecithin/chitosan paste is then introduced into the warm water and mixed strongly until the paste transforms into small granules with a typical size of 1 to 2 millimeters. The granules are filtered and dried in air to yield a free-flowing and non-sticky product. The product then can be added to a skin care formulation in sufficient quantity (1 to 90 wt.%, preferably 5 to 75 wt.%, more preferably 10 to 50 wt.%) to assure transfer of the formulation onto the animal's skin. In modification to this approach, the lecithin/chitosan paste can be extruded into cold water resulting in the formation of rods or pellets of any desired size and dimensions.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

All patents and other references mentioned above are incorporated in full herein by this reference, the same as if set forth at length.

WHAT IS CLAIMED AS NEW AND DESIRED TO BE SECURED BY LETTERS PATENT OF THE UNITED STATES IS:

1. A composition comprising

(a) 0.25 to 25 wt.%, based on the total weight of (a) and (b), of one or more transfer agents; and

(b) 75 to 99.75 wt.%, based on the total weight of (a) and (b), of one or more barrier materials.

2. A composition, comprising:

(a′) 65 to 99.75 wt.%, based on the total weight of (a′) and (b′), of one or more barrier materials; and

(b′) 0.25 to 35 wt.%, based on the total weight of (a′) and (b′), of a mixture, said mixture comprising:

(b″) 0.25 to 99.99 wt.%, based on the total weight of (b″) and (b‴), of one or more transfer agents; and

(b‴) 0.01 to 99.75 wt.%, based on the total weight of (b″) and (b‴), of at least one skin care active agent,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition.

3. The composition of Claim 2, wherein said skin care active agent is selected from the group consisting of

Acetic Acid

Aclometasone Dipropionate

Acyclovir

Alclometasone Dipropionate

Aluminum Chlorhydrate

Aluminum Chlorhydroxide

Aluminum Chloride Hexahydrate

Amcinonide

Aminobenzoate Potassium

Ammonium Lactate

Ammonium Mercury

Amphotericin B

Anthralin

Antimicrobial Agents

Bacitracin

Balsam Peru

Benzocaine

Benzoin Compoundecylenate

Benzoyl Peroxide (BPO)

Beta-Carotene

Betamethasone Acetate

Betamethasone Dipropionate

Betamethasone Sodium Phosphate

Betamethasone Valerate

Butaconazole Nitrate

Butamben Picrate

Canthardin

Carbol Fuchsin

Castor Oil

Cetylpyridinium Chloride

Chloramphenicol

Chlorcyclizine

Chlorhexidine

Chlorhexidine Acetate

Chlorhexidine Gluconate

Chloroxine

Chloroxynol

Ciclopirox Olamine

Clindamycin HCl

Clioquinol

Clobetasol Propionate

Clocortolone Pivalate

Clotrimazole

Coal Tar

Collagenase

Cortisone

Cortisone Acetate

Crotamiton

Cyclopentolate HCl

Dapsone

Desonide

Desoxymetasone

Desoxyribonuclease

Dexamethasone

Dexamethasone Acetate

Dexamethasone Sodium Phosphate

Dibucaine

Dichloroacetic Acid

Dichlorophene

Diflorasone Diacetate

Diperodon

Econazole Nitrate

Ephedrine HCl

Erythromycin

Estradiol

Etretinate

Fibrinolysin

Flucinolone

Flucinolone Acetonide

Fluocinonide

Fluorouracil

Fluradrenolone

Flurandrenolide

Fluticasone Propionate

Formaldehyde

Gentamycin Sulfate

Gramicid

Griseofulvin

Guaifenesin

Halcinonide

Halobetasol Propionate

Haloprogin

Hexachlorophene

Hexetadine

Hyaluronidase

Hydrocodone

Hydrocortisone

Hydrocortisone Acetate

Hydrocortisone Butyrate

Hydrocortisone Sodium Phosphate

Hydrocortisone Sodium Succinate

Hydrocortisone Valerate

Hydroquinone

Hydroxyzine HCl

Hydroxyzine Pamoate

Iodine

Iodochlorhydrocodone

Iodoquinol

Isotretinoin

Ketoconazole

Lactic Acid

Lecithin

Lidocaine Hydrochloride

Lindane

Mafenide Acetate

Meclocycline Sulfosalicylate

Methoxsalen

Methylprednisone

Methylprednisone Acetate

Methylprednisone Sodium Succinate

Metronidazole

Miconazole Nitrate

Minoxidil

Mometasone Furoate

Monobenzone

Mupriocin

Naftifine HCl

Neomycin Sulfate

Nitrofurazone

Nystatin

Octyl Methoxycinnamate

Oxybenzone

Oxyquinoline Sulfate

Papain

para-Aminobenzoic Acid

Permethrin

Phentermine HCl

Podophylum

Polymyxin B Sulfate

Potassium Iodide

Pramoxine HCl

Prednicarbate

Prednisolone Sodium Phosphate

Prednisone

Pseudoephedrine

Pyrogallic Acid

Retinoic Acid

Retinol

Salicylic Acid

Saluminum Acid

Scarlet Red

Selenium Sulfide

Silver Nitrate

Silver Sulfadiazine

Sodium Sulfacetimide

Sodium Thiosulfate

Streptokinase

Sulconazole

Sulconazole Nitrate

Sulfabenzamide

Sulfacetamide

Sulfanilamide

Sulfathiazole

Sulfur

Sunscreen Agents

Sutilains

Terconazole

Tetracaine

Tetracycline

Tretinoin

Triacetin

Triamcinolone

Triamcinolone Acetonide

Triamcinolone Diacetate

Trimeprazine Tartrate

Trioxsalen

Triple Dye

Trypsin

Undecylenic Acid

Urea

Vitamins (all)

Zinc Oxide

Zinc Undecylenate

and other agents known in the art to have medical, cosmetic, or other effects on the skin.

4. A method for forming a protective barrier on skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(a) 0.25 to 25 wt.%, based on the total weight of (a) and (b), of transfer agent; and

(b) 75 to 99.75 wt.%, based on the total weight of (a) and (b), of a barrier material.

5. A method for cleaning and removing contaminants from the skin

while forming a protective barrier on skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(a) 0.25 to 25 wt.%, based on the total weight of (a) and (b), of a transfer agent; and

(b) 75 to 99.75 wt%, based on the total weight of (a) and (b), of a barrier material.

6. A method for applying a skin care agent to skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(a') 65 to 99.75 wt.%, based on the total weight of (a') and (b'), of one or more barrier materials; and

(b') 0.25 to 35 wt.%, based on the total weight of (a') and (b'), of a mixture, said mixture comprising:

(b'') 0.25 to 99.99 wt.%, based on the total weight of (b'') and (b'''), of one or more transfer agents; and

(b''') 0.01 to 99.75 wt.%, based on the total weight of (b'') and (b'''), of at least one skin care agent,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition.

7. A method for cleaning and removing contaminants from the skin while applying a skin care agent to skin, said method comprising applying an effective amount of composition to skin, said composition comprising:

(a') 65 to 99.75 wt.%, based on the total weight of (a') and (b'), of one or more barrier materials; and

(b') 0.25 to 35 wt.%, based on the total weight of (a') and (b'), of a mixture, said mixture comprising:

(b") 0.25 to 99.99 wt.%, based on the total weight of (b") and (b'"), of one or more transfer agents; and

(b'") 0.01 to 99.75 wt.%, based on the total weight of (b") and (b'"), of at least one skin care agent,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition.

8. A composition which comprises:

(1) 25 to 80 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 1 to 50 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 20 to 50 wt.%, based on the total weight of (1), (2), and (3), of water.

9. The composition of claim 8, which comprises:

(1) 30 to 60 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 10 to 40 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 30 to 40 wt.%, based on the total weight of (1), (2), and (3), of water.

10. A method for forming a protective barrier on skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(1) 25 to 80 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 1 to 50 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 20 to 50 wt.%, based on the total weight of (1), (2), and (3), of water.

11. A method for cleaning and removing contaminants from the skin while performing a protective barrier on skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(1) 25 to 80 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 1 to 50 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 20 to 50 wt.%, based on the total weight of (1), (2), and (3), of water.

12. The method of Claim 10 or 11, wherein said composition comprises:

(1) 30 to 60 wt.%, based on the total weight of (1), (2), and (3), of a barrier material;

(2) 10 to 40 wt.%, based on the total weight of (1), (2), and (3), of lecithin; and

(3) 30 to 40 wt.%, based on the total weight of (1), (2), and (3), of water.

13. A composition which comprises:

(i) 1 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 10 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 1 to 50 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan.

14. The composition of Claim 13, which comprises:

(i) 5 to 25 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 15 to 25 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 10 to 40 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan.

15. A method for forming a protective barrier on skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(i) 1 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 10 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 1 to 50 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan.

16. A method for cleaning and removing contaminants from the skin while forming a protective barrier on skin, said method comprising applying an effective amount of a composition to skin, said composition comprising:

(i) 1 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 10 to 30 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 1 to 50 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan.

17. The method of Claim 15 or 16, wherein said composition comprises:

(i) 5 to 25 wt.%, based on the total weight of (i), (ii), and (iii), of lecithin;

(ii) 15 to 25 wt.%, based on the total weight of (i), (ii), and (iii), of a barrier material; and

(iii) 10 to 40 wt.%, based on the total weight of (i), (ii), and (iii), of chitosan.

18. A method for forming a hydrophobic barrier on a surface, comprising applying to said surface an effective amount of a composition comprising:

(a) 0.25 to 25 wt.%, based on the total weight of (a) and (b), of one or more transfer agents; and

(b) 75 to 99.75 wt.%, based on the total weight of (a) and (b), of one or more barrier materials.

19. A method for cleaning and removing contaminants from a surface while forming a hydrophobic barrier on a surface, comprising applying to said surface an effective amount of a composition comprising:

(a) 0.25 to 25 wt.%, based on the total weight of (a) and (b), of one or more transfer agents; and

(b) 75 to 99.75 wt.%, based on the total weight of (a) and (b), of one or more barrier materials.

20. The method of Claim 18 or 19, wherein said surface is selected from the group consisting of molds, ship hulls, leather, automobile surfaces, wood, metal, painted surfaces, floors, walls, billboards, train cars, paper, cardboard, pots, pans, cooking utensils, glass, china, plant foliage, polymers, plastics, fiberglass, fabrics, resins, composites including carbon fiber and graphitic materials, and mineral substrates.

21. A method for forming a hydrophobic barrier on a surface, comprising applying to said surface an effective amount of a composition, comprising:

(a′) 65 to 99.75 wt.%, based on the total weight of (a′) and (b′), of one or more barrier materials; and

(b′) 0.25 to 35 wt.%, based on the total weight of (a′) and (b′), of a mixture, said mixture comprising:

(b″) 0.25 to 99.99 wt.%, based on the total weight of (b″) and (b‴), of one or more transfer agents; and

(b‴) 0.01 to 99.75 wt.%, based on the total weight of (b″) and (b‴), of at least one active agent,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition.

22. A method for cleaning and removing contaminants from a surface while forming a hydrophobic barrier on a surface, comprising applying to said surface an effective amount of a composition, comprising:

(a') 65 to 99.75 wt.%, based on the total weight of (a') and (b'), of one or more barrier materials; and

(b') 0.25 to 35 wt.%, based on the total weight of (a') and (b'), of a mixture, said mixture comprising:

(b") 0.25 to 99.99 wt.%, based on the total weight of (b") and (b'"), of one or more transfer agents; and

(b'") 0.01 to 99.75 wt.%, based on the total weight of (b") and (b'"), of at least one active agent,

provided said transfer agent is present in said composition in an amount of at least 0.25 wt.%, based on the total weight of said composition.

23. The method of Claim 21 or 22, wherein said surface is selected from the group consisting of molds, ship hulls, leather, automobile surfaces, wood, metal, painted surfaces, floors, walls, billboards, train cars, paper, cardboard, pots, pans, cooking utensils, glass, china, plant foliage, polymers, plastics, fiberglass, fabrics, resins, composites including carbon fiber and graphitic materials, and mineral substrates.

PCT

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(54) Title: COMPOSITIONS AND METHODS OF USING THE SAME

(57) Abstract

The present invention discloses compositions containing a one or more transfer agents and one or more barrier materials which form, upon application to a substrate, even a wet substrate or substrate immersed under water, adhesive, protective barriers. The compositions may be modified to provide an appropriate viscosity and other characteristics and may serve as a carrier for active agents.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/30003

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : A61K 7/00; A61F 13/00; A01N 25/00
US CL :424/401, 405, 422
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/401, 405, 422

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN: USPATFULL, CAPLUS
search terms: lecithin, chitosan, was, polydimethylsiloxane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,686,087 A (ANSMANN et al.) 11 November 1997, see column 4.	1-3, 6, 8, 9, 13, 14 --- 4, 10, 15, 18, 21
X --- Y	US 5,665,333 A (HOMOLA et al.) 09 September 1997, see entire document.	1-3, 18-23 --- 4-17

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 22 MAY 2000	Date of mailing of the international search report 21 JUN 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ALYSIA BERMAN Telephone No. (703) 308-0196

Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATION[redacted]SEARCH REPORT

Interm[redacted]l application No.
PC[redacted]99/30003

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because thev relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/[redacted]/30003

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-3, 8, 9, 13 and 14, drawn to a composition.
Group II, claim(s) 4, 6, 10, 12, 15, 17, 18, 20, 21 and 23, drawn to a method for forming a hydrophobic barrier on a surface.
Group III, claim(s) 5, 7, 11, 12, 16, 17, 19, 20, 22 and 23, drawn to a method for cleaning and removing contaminants from a surface while forming a hydrophobic barrier on a surface.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid.

If applicant elects to pay additional fees for Group II, the species are as follows:

A. A method of forming a protective barrier on the skin.

B. A method for forming a protective barrier on molds, ship hulls, leather, automobile surfaces, wood, metal, painted surfaces, floors, walls, billboards, train cars, paper, cardboard, pots, pans, cooking utensils, glass, china, plant foliage, polymers, plastics, fiberglass, fabrics, resins, composites including carbon fiber and graphitic minerals, and mineral substrates.

If applicant elects to pay additional fees for Group III, the species are as follows:

C. A method for cleaning and removing contaminants from the skin while forming a protective barrier on the skin.

D. A method for cleaning and removing contaminants while forming a hydrophobic barrier on molds, ship hulls, leather, automobile surfaces, wood, metal, painted surfaces, floors, walls, billboards, train cars, paper, cardboard, pots, pans, cooking utensils, glass, china, plant foliage, polymers, plastics, fiberglass, fabrics, resins, composites including carbon fiber and graphitic minerals, and mineral substrates.

The claims are deemed to correspond to the species listed above in the following manner:

Species A - claims 4, 6, 10, 12, 15 and 17.
Species B or D - claims 20 and 23.
Species C - claims 5, 7, 11, 12, 16 and 17.

The following claims are generic: 18, 19, 21 and 22.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical feature which is the combination of a transfer agent and a barrier material is known in the art as evidenced by US Patent 5,665,333. See the claims.

The inventions listed as Groups I and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical feature which is the combination of a transfer agent and a barrier material is known in the art as evidenced by US Patent 5,665,333. See the claims.

The inventions listed as Groups II and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical feature which is the combination of a transfer agent and a barrier material is known in the art as evidenced by US Patent 5,665,333. See the claims.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons: the special

technical feature which is the combination of a transfer agent and a barrier material is known in the art as evidenced by US Patent 5,665,333. See the claims.